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⑤④ Process for bleaching of lignocellulose-containing pulp.

⑤⑦ The present invention relates to a process for delignification and bleaching of chemically digested lignocellulose-containing pulp, wherein the pulp is acid treated at a pH of between about 1 and about 6, whereupon a water-soluble compound containing an alkaline earth metal is added at a pH of between about 1 and about 7 before the pulp is treated with a chlorine-free bleaching agent. The chlorine-free bleaching agent includes peroxide compounds, ozone, oxygen and sodium dithionite in an optional sequence or mixture. After the treatment according to the invention, the pulp may be finally bleached to the desired brightness, suitably with a chlorine-free bleaching agent, such as ozone, to completely avoid formation and discharge of AOX.

The present invention relates to a process for delignification and bleaching of chemically digested lignocellulose-containing pulp, wherein the pulp is acid treated at a pH of between about 1 and about 6, whereupon a water-soluble compound containing an alkaline earth metal is added at a pH of between about 1 and about 7 before the pulp is treated with a chlorine-free bleaching agent. The initial acidic treatment
 5 removes the trace metals of the pulp, whereas the subsequent addition of alkaline earth metal ions in aqueous solution returns the ions to the positions in the pulp where they have a particularly beneficial effect on the preservation of the cellulose chains and, consequently, on the viscosity, as well as on the consumption of bleaching agent in the subsequent bleaching step. After the treatment according to the invention, the pulp may be finally bleached to the desired brightness, suitably with a chlorine-free bleaching
 10 agent, such a ozone, to completely avoid formation and discharge of AOX.

Background

In the production of chemical pulp of high brightness, wood chips are first cooked to separate the
 15 cellulose fibres. Part of the lignin holding the fibres together is thus degraded and modified, such that it can be removed by subsequent washing. However, in order to obtain sufficient brightness, more lignin has to be removed, together with brightness-impairing (chromophoric) groups. This is frequently effected by delignification with oxygen, followed by bleaching in several stages.

For environmental reasons, it has become increasingly common to treat chemical pulp with chlorine-free bleaching agents already in the first bleaching steps. The big advantage is the drastic reduction in the discharges of chlorinated organic substances detrimental to the environment, owing to the combined effect of a smaller amount of chlorine-containing bleaching agents and lower content of lignin, which is the organic substance primarily reacting with the chlorine.

It is known to use chlorine-free bleaching agents, such as hydrogen peroxide, peracetic acid or ozone, already in the prebleaching. However, the delignification and consumption of the bleaching agent become less effective than with chlorine-containing bleaching agents, unless the pulp is pretreated. Thus, a hydrogen peroxide treatment in an alkaline environment is disturbed by the presence in the pulp of ions of certain metals, such as Mn, Cu and Fe. These metal ions cause degradation of hydrogen peroxide, thereby reducing the efficiency of the peroxide treatment and increasing the consumption of peroxide. According to
 25 CA 1,206,704, this can be counteracted by pretreating the pulp with an acid, such as sulphuric acid or nitric acid, whereby the concentration of all types of metal ions is reduced. However, by this treatment also metal ions, for example Mg, which are advantageous to the peroxide treatment disappear, which ions stabilize the peroxide and increase the selectivity of the peroxide.

CA 575,636 discloses the addition of magnesium sulphate to stabilize alkaline peroxide solutions.
 35 However, the addition is made directly to the bleaching liquor and in alkaline environment insoluble magnesium hydroxide precipitates. Furthermore, US 4,222,819 discloses the addition of magnesium ions to acidic peroxide solutions, but also in this case the addition is made directly to the bleaching liquor. None of the related methods makes possible diffusion of the magnesium ions into the pulp to such an extent, that a pulp of high brightness and strength can be obtained.

The invention

The invention provides a process in which lignocellulose-containing pulp is treated under the conditions disclosed in the claims, whereby the metal ions harmful to the subsequent bleaching are effectively
 45 removed and the profile of alkaline earth metals is restored before the pulp is bleached in a chlorine-free bleaching step.

The invention relates to a process for bleaching of chemically digested lignocellulose-containing pulp, wherein the pulp is acid treated at a pH in the range from about 1 up to about 6, whereupon a compound containing an alkaline earth metal is added at a pH in the range from about 1 up to about 7 and in an
 50 amount of from about 0.01 kg, suitably 0.5 kg, up to about 10 kg/ton of dry pulp, calculated as alkaline earth metal, and that the pulp subsequently is treated with a chlorine-free bleaching agent.

Acid treatment is an effective process to eliminate metal ions from lignocellulose-containing pulps. At the same time it is known, that ions of alkaline earth metals, especially when in their original positions in the pulp, have a positive influence on the selectivity of the delignification as well as on the stability and
 55 consumption of chlorine-free bleaching agents, such as peroxides, ozone and oxygen. The present process presents an economic solution to the problem of creating a suitable trace-metal profile for the subsequent chlorine-free bleaching, in that non-desirable metal ions are eliminated while supplied ions of alkaline earth metals essentially recover the positions in the vicinity of the cellulose chains previously occupied by ions of

alkaline earth metals. This is achieved by adding the compound containing an alkaline earth metal at such a pH and such a temperature that the compound is dissolved in water, thus enabling the diffusion required to obtain the intended effect. Furthermore, an advantage of the present process is that the pH adjustment between the treatment with acid and addition of alkaline earth metal ions becomes very limited or may be left out altogether, which is advantageous to process technique and economy.

Chlorine-free bleaching agents include inorganic peroxide compounds, such as hydrogen peroxide and sodium peroxide, organic peroxide compounds, such as peracetic acid, as well as ozone, oxygen and sodium dithionite. Suitably, hydrogen peroxide (P), oxygen (O) and ozone (Z) are used in an optional sequence or mixture. Preferably, use is made of hydrogen peroxide or mixtures of hydrogen peroxide and oxygen (PO). The sequence P-Z or (PO)-Z are especially preferred.

In the treatment with a chlorine-free bleaching agent in an alkaline environment, pH is suitably adjusted by adding to the pulp an alkali or an alkali-containing liquid, such as sodium carbonate, sodium hydrogen carbonate, sodium hydroxide, oxidized white liquor or magnesium hydroxide slurry. Suitably, the magnesium hydroxide slurry is taken from the chemical handling system in the production of sulphite pulp with magnesium as base, i.e. magnesite pulp.

The acid treatment suitably is carried out with an acid. The acids used are inorganic acids, suitably sulphuric acid, nitric acid, hydrochloric acid or residual acid from a chlorine dioxide reactor, either separately or in an optional mixture. Preferably, sulphuric acid is employed.

Compounds containing an alkaline earth metal relate to water-soluble chemicals containing magnesium or calcium, or mixtures of such chemicals. Use is suitably made of magnesium-containing compounds, such as magnesium sulphate or magnesium chloride, or calcium-containing compounds, such as calcium chloride or calcium oxide. Use is preferably made of magnesium sulphate or magnesium chloride, the use of magnesium sulphate being especially preferred. The combination of temperature and pH at the addition of the compound containing an alkaline earth metal is always so chosen that the compound is in aqueous solution when contacted with the pulp.

In the process according to the invention, the acid treatment is carried out at a pH of from about 1 up to about 6, suitably from 1.5 up to 5, preferably from 2 up to 4. It is especially preferred that the acid treatment is carried out at a pH of from 2 up to 3. When magnesium is the alkaline earth metal in the compound containing an alkaline earth metal, the addition is made at a pH in the range from about 1 up to about 7, suitably in the range from 2 up to 6, preferably in the range from 2 up to 4. It is especially preferred that the addition of magnesium is made at a pH of from 2 up to 3. When the chlorine-free bleaching agent is hydrogen peroxide, the pulp is suitably treated at a pH of from about 8 up to about 12, preferably at a pH of from 10 up to 12. Treatment with the other chlorine-free bleaching agents mentioned above, is carried out within the normal pH ranges for each bleaching agent, which are well-known to the person skilled in the art.

The treatment according to the invention is preferably carried out with a washing step between the acid treatment and addition of alkaline earth metal ions, such that the trace metals that are harmful to the treatment with a chlorine-free bleaching agent are removed from the pulp suspension.

The realization of the acid treatment, a compound containing an alkaline earth metal and a chlorine-free bleaching agent, can be carried out at an optional position in the bleaching sequence, e.g. immediately after digestion of the pulp or after an oxygen step. The process according to the invention is preferably applied to pulp that has been delignified in an oxygen step prior to the treatment.

It is also within the scope of the invention, that the pulp in the acid treatment also can be subjected to bleaching and/or delignifying treatment. Bleaching and/or delignifying chemicals active within the pH range suitable in the acid treatment, are e.g. chlorine dioxide, ozone, peracetic acid and/or an acid peroxide-containing compound. Suitably, a combination of acid treatment and bleaching and/or delignifying treatment takes place in an ozone step.

Lignocellulose-containing pulps relate to chemical pulps of softwood and/or hardwood digested according to the sulphite, sulphate, soda or organosolv process, or modifications and/or combinations thereof. Use is suitably made of softwood and/or hardwood digested according to the sulphate process, preferably sulphate pulp of hardwood.

The treatment according to the invention can be applied to lignocellulose-containing pulps having an initial kappa number within the range from about 5 up to about 40, suitably 7 up to 32, preferably from 10 up to 20. Here, the kappa number is determined according to the standard method SCAN-C 1:77.

In the process according to the invention, the acid treatment is carried out at a temperature of from about 10 up to about 95 °C, suitably from 20 up to 80 °C and preferably from 40 up to 80 °C, and for a period of time of from about 1 up to about 120 min, suitably from 10 up to 120 min and preferably from 20 up to 40 min. The compound containing an alkaline earth metal is added at a temperature of from about 10

up to about 95 °C, preferably from 40 up to 80 °C, and for a period of time of from about 1 up to about 180 min, preferably from 20 up to 180 min and preferably from 30 up to 120 min. When the chlorine-free bleaching agent is hydrogen peroxide, the pulp is treated at a temperature of from about 30 up to about 100 °C, preferably from 60 up to 90 °C, and for a period of time of from about 30 up to about 300 min, suitably from 60 up to 240 min. In the acid treatment and in the addition of alkaline earth metal ions, the pulp concentration may be from about 3 up to about 35% by weight, preferably from 3 up to 15% by weight. When the chlorine-free bleaching agent is hydrogen peroxide, the pulp concentration may be from about 3 up to about 50% by weight, suitably from 3 up to 35% by weight and preferably from 10 up to 25% by weight. Treatment with the other chlorine-free bleaching agents mentioned above, is carried out within the normal ranges of temperature, time and pulp concentration for each bleaching agent, which are well-known to the person skilled in the art.

The amount of compound containing an alkaline earth metal charged, lies in the range from about 0.01 up to about 10 kg/ton of dry pulp, calculated as alkaline earth metal, suitably in the range from 0.5 up to 5 kg/ton of dry pulp, calculated as alkaline earth metal, and preferably in the range from 2 up to 4 kg/ton of dry pulp, calculated as alkaline earth metal.

In preferred embodiments employing hydrogen peroxide as the chlorine-free bleaching agent, the amount of hydrogen peroxide, lies in the range from about 2 up to about 50 kg/ton of dry pulp, calculated as 100% hydrogen peroxide. The upper limit is not critical, but has been set for reasons of economy. The amount of hydrogen peroxide suitably lies in the range from 3 up to 30 kg/ton of dry pulp and preferably from 4 up to 20 kg/ton of dry pulp, calculated as 100% hydrogen peroxide.

After the acid treatment, a compound containing an alkaline earth metal and a chlorine-free bleaching agent, the pulp can be used for direct production of paper with a lower demand of brightness. Alternatively, the pulp may be finally bleached to the desired higher brightness, by treatment in one or more steps. Suitably, the final bleaching is also carried out with chlorine-free bleaching agents of the type mentioned above, optionally with intermediate alkaline extraction steps, which may be reinforced with peroxide and/or oxygen. In this way, the formation and discharge of AOX is completely eliminated. Suitably, the final bleaching is carried out with ozone in one or more steps. By the treatment according to the invention, the lignin content has been reduced to a sufficiently low level before any chlorine-containing bleaching agents are used. Therefore, chlorine dioxide and/or hypochlorite may well be used in one or more final bleaching steps without causing formation of large amounts of AOX.

Moreover, use of the process according to the invention means that the brightness and kappa number of the resulting pulp is higher and lower, respectively, than with the processes in which a compound containing an alkaline earth metal is not added at all or is added at a higher pH. In a process for bleaching chemical pulps, the aim is a high brightness as well as a low kappa number, the latter meaning a low content of undissolved lignin. At the same time, the consumption of the chlorine-free bleaching agent should be as low as possible meaning lower treatment costs. In the process according to the invention, these objects are met, as is apparent from the Examples. Furthermore, the strength of the pulp, measured as viscosity, is sufficient, which means that the pulp contains cellulose chains which are long enough to give a strong product.

The invention and its advantages are illustrated in more detail by the Examples below which, however, are only intended to illustrate the invention and are not intended to limit the same. The percentages and parts stated in the description, claims and examples, refer to percent by weight and parts by weight, respectively, unless anything else is stated.

Example 1

Sulphate pulp of softwood having a kappa number of 17, a brightness of 35% ISO and a viscosity of 970 dm³/kg was treated with sulphuric acid at a pH of 2.0. The pulp was treated at a temperature of 60 °C for 30 min, the pulp concentration being 10% by weight. After washing the pulp with water, magnesium was added in the form of an aqueous solution containing MgSO₄, to give a concentration of magnesium in the pulp of at least 500 ppm. In the tests, the pH at the time of the addition was varied between 2.3 and 11.5 by addition of sulphuric acid. Then, the pulp was bleached with hydrogen peroxide at a temperature of 90 °C, the residence time and pulp concentration being 180 min and 15% by weight, respectively. The final pH was 11.5, and the addition of hydrogen peroxide was 15 kg/ton of dry pulp, calculated as 100% hydrogen peroxide. For comparative purposes, magnesium was added directly to the hydrogen peroxide step under the conditions stated above, in accordance with the prior art. To provide a further comparison, the pulp was also treated with only sulphuric acid and hydrogen peroxide under the conditions stated above. The kappa number, viscosity and brightness of the pulp were determined according to SCAN Standard Methods, and

the consumption of hydrogen peroxide was determined by iodometric titration. The test results appear from the Table below.

TABLE I

pH at the addition of Mg	Kappa number step 2	Viscosity step 2 (dm ³ /kg)	Brightness step 2 (% ISO)	Residual H ₂ O step 2 (kg/ton)
2.3	9.1	903	61.0	1.5
4.7	9.2	910	60.0	1.0
9.5	9.8	930	56.1	0.9
11.5	10.0	940	52.2	0.2
---- *	9.8	890	54.1	0.5
2.3 **	9.9	875	48.2	0.0

* Magnesium added directly to the alkaline hydrogen peroxide step.

** No magnesium added.

As is apparent from the Table, the treatment according to the present invention with MgSO₄ at a pH in the range from about 2 up to about 6 is essential to give maximum increase in brightness and maximum reduction of the kappa number, as well as minimum decrease in viscosity and minimum consumption of hydrogen peroxide. Furthermore, the importance of the magnesium ions for the increase in brightness appears from the comparison at a pH of 2.3, where, in the final test, the peroxide treatment was preceded only by acidic treatment.

Example 2

Oxygen-delignified sulphate pulp of softwood having a kappa number of 13.7, a brightness of 37.1% ISO and a viscosity of 1057 dm³/kg, was treated in a first step with 15 kg of sulphuric acid/ton of dry pulp at a pH of 1.9. The pulp was treated at a temperature of 50 °C for 60 min, the pulp concentration being 10% by weight. After washing the pulp with water, in a second step between 0.1 and 1.5 kg of magnesium/ton of dry pulp was added in the form of an aqueous solution containing MgSO₄. Magnesium was added at a pH of 4.1, a temperature of 50 °C for 60 min and with a pulp concentration of 3.5% by weight. Then, the pulp was bleached with hydrogen peroxide at a temperature of 90 °C, the residence time and pulp concentration being 240 min and 10% by weight, respectively. The final pH was 11.5 and the addition of hydrogen peroxide was 20 kg/ton of dry pulp calculated as 100% hydrogen peroxide. For comparative purposes, the pulp was also treated with only sulphuric acid and hydrogen peroxide under the conditions stated above. The kappa number, viscosity and brightness were determined according to SCAN Standard Methods. The results after bleaching with hydrogen peroxide appear from the Table below.

TABLE II

Amount of Mg added in step 2 (kg/ton)	Amount of Mg in pulp after step 2 (ppm)	Kappa no. step 3	Viscosity step 3 (dm ³ /kg)	Brightness step 3 (% ISO)
0	3,7	9.6	900	51.5
0.1	130	8.2	870	61.8
0.3	250	7.8	864	65.1
0.75	370	7.7	855	65.9
1.5	480	7.6	845	67.3

As is apparent from the Table, acid treatment followed by addition of dissolved magnesium and bleaching with hydrogen peroxide according to the present invention, positively influence the pulp as regards kappa number, viscosity and brightness.

Example 3

The oxygen-delignified sulphate pulp of softwood used in Example 2, was treated in the sequences D -

EOP-Z - P (test 1) and D - EOP - Z - Mg - P (test 2), where the conditions in each step were equal in both sequences. D and EOP relate to a conventional chlorine dioxide step and a conventional alkaline extraction step reinforced with hydrogen peroxide and oxygen, respectively. Z relates to an ozone step with a pH of 2.3. Mg relates to the addition of 1 kg of magnesium/ton of dry pulp, in the form of an aqueous solution containing MgSO_4 . Magnesium was added at a pH of 4.1, a temperature of 50°C for 30 min, the pulp concentration being about 3% by weight. P relates to a hydrogen peroxide step, where the pulp was treated at a temperature of 80°C for 120 min. The final pH was about 11.5 and the addition of hydrogen peroxide was 5 kg/ton of dry pulp calculated as 100% hydrogen peroxide. The viscosity and brightness were determined according to SCAN Standard Methods. The results after bleaching with hydrogen peroxide appear from the Table below.

TABLE III

Test	Amount of Mg added (kg/ton)	Amount of Mg in pulp after addition (ppm)	Viscosity (dm^3/kg)	Brightness (% ISO)
1	0	16	820	86.3
2	1.0	255	872	88.4

As is apparent from the Table, addition of dissolved magnesium after an initial acid treatment with ozone and bleaching with hydrogen peroxide according to the present invention, positively influence the pulp as regards viscosity and brightness.

Example 4

The oxygen-delignified sulphate pulp of softwood used in Example 2, was treated in the sequences Step1 - P_1 - Z - P_2 (test 1) and Step1 - P_1 - Z - Mg - P_2 (test 2), where the conditions in each step were equal in both sequences. Step1 relates to treatment with EDTA at a pH of 5. Z relates to an ozone step with a pH of 2.3, the pulp concentration being 10% by weight. Mg relates to the addition of 1 kg of magnesium/ton of dry pulp, in the form of an aqueous solution containing MgSO_4 . Magnesium was added at a pH of 4.1, a temperature of 50°C for 30 min, the pulp concentration being about 3% by weight. P_2 relates to a hydrogen peroxide step, where the pulp was treated at a temperature of 80°C for 120 min. The final pH was about 11.5 and the addition of hydrogen peroxide was 5 kg/ton of dry pulp calculated as 100% hydrogen peroxide. For comparative purposes, the pulp was also treated in the sequence Step1 - P_1 - z - (PMg) (test 3). (PMg) relates to the addition of magnesium in the second alkaline hydrogen peroxide step under the conditions stated above, in accordance with the prior art. The viscosity and brightness were determined according to SCAN Standard Methods, and the consumption of hydrogen peroxide was determined by iodometric titration. The results after the second hydrogen peroxide step appear from the Table below.

TABLE IV

Test	Amount of Mg added (kg/ton)	Amount of Mg in pulp (ppm)	Viscosity (dm^3/kg)	Bright-ness (% ISO)	H_2O_2 consumed in P_2 (% of added)
1	0	9	794	80.9	76
2	1.0	300	856	83.9	28
3	1.0	120	809	81.6	60

As is apparent from the Table, addition of magnesium within the present pH range before bleaching with hydrogen peroxide, positively influence the pulp as regards viscosity and brightness and reduces the consumption of hydrogen peroxide.

Claims

1. A process for delignification and bleaching of chemically digested lignocellulose-containing pulp, characterised in that the pulp is acid treated at a pH in the range from about 1 up to about 6,

whereupon a compound containing an alkaline earth metal is added at a pH in the range from about 1 up to about 7 and in an amount of from about 0.01 up to about 10 kg/ton of dry pulp, calculated as alkaline earth metal, and that the pulp subsequently is treated with a chlorine-free bleaching agent.

- 5 2. A process according to claim 1, **characterised** in that the chlorine-free bleaching agent consists of hydrogen peroxide, oxygen and ozone in an optional sequence or mixture.
3. A process according to claim 2, **characterised** in that the chlorine-free bleaching agent consists of hydrogen peroxide or a mixture of hydrogen peroxide and oxygen.
- 10 4. A process according to claim 1, **characterised** in that the compound containing an alkaline earth metal is added at a pH of from 2 up to 6.
- 15 5. A process according to claim 1, **characterised** in that the compound containing an alkaline earth metal consists of a water-soluble magnesium compound.
6. A process according to claim 1 or 5, **characterised** in that the compound containing an alkaline earth metal consists of magnesium sulphate or magnesium chloride.
- 20 7. A process according to claim 1, **characterised** in that the pulp is washed after the acid treatment.
8. A process according to claim 1, **characterised** in that the pulp, after the treatment, is finally bleached with a chlorine-free bleaching agent, optionally with intermediate alkaline extraction steps.
- 25 9. A process according to claim 8, **characterised** in that the pulp, after the treatment, is finally bleached with ozone in one or more steps.
- 30 10. A process according to claims 1-9, **characterised** in that the acid treatment is carried out at a temperature of from about 10 up to about 95°C for about 1 up to about 120 min, that the compound containing an alkaline earth metal is added at a temperature of from about 10 up to about 95°C for about 1 up to about 180 min and in an amount of from 0.5 up to 5 kg/ton of dry pulp, calculated as alkaline earth metal, the treated pulp having a concentration of from about 3 up to about 35% by weight, and that the pulp is treated with hydrogen peroxide at a pH of from about 8 up to about 12.

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EUROPEAN SEARCH REPORT

Application Number

EP 92 20 1005

DOCUMENTS CONSIDERED TO BE RELEVANT

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-3 507 744 (KIMBERLY-CLARK CORPORATION) * column 2, line 66 - column 3, line 16; example 3 * ---	1-3, 7, 8, 10	D21C9/10 D21C9/153 D21C9/16
A	WORLD PATENTS INDEX LATEST Week 9118, Derwent Publications Ltd., London, GB; AN 91-127527 & JP-A-3 064 589 (MITSUBISHI GAS CHEM KK) 19 March 1991 * abstract * ---	1-3, 5, 6, 8, 10	
A	DE-A-2 022 866 (MO OCH DOMSJÖ AB) * page 10, line 15 - line 30; claims * -----	1, 2, 5-8	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			D21C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 08 JULY 1992	Examiner BERNARDO NORIEGA F.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	